PATENT SPECIFICATION

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A5E 1A3B 1A5B2 1C15B1 1C15B2 1C15B3 1C15D1 1C15D2 1C15D3 1C8B

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(54) NAPHTHOQUINONES AND THEIR USE AS PESTICIDES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

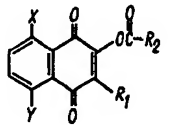
This invention relates to miticidal and aphicidal compounds which are 2-higher alkyl-3-hydroxy-1,4-naphthoquinone carboxylic acid esters.

U.S Patents 2,553,647 and 2,553,648 disclose broadly 2-higher alkyl-3-acetoxy-1,4-naphthoquinones and their corresponding ester derivatives. These compounds are described as having antagonistic action against organisms which cause malarial infections.

U.S. Patent 2,572,946 discloses the use of non-acylated compounds as miticides; it contains no teaching of acylated compounds.

Nakanishi *et al JACS* 1952, 3910—3915 discloses the *n*-undecyl analog of 2-alkyl-3-acetoxy-1,4-naphthoquinone. No use for the composition is disclosed.

According to this invention there is provided a method for controlling mites or aphids which comprises applying to a locus infested or liable to be infested with said mites or aphids an effective amount of a compound of the general formula:



(I)

where

R_1 = alkyl of 8—14 carbon atoms either branched, cyclic, or straight chained;
R_2 = alkyl of 1—17 carbon atoms either branched or straight chained, alkenyl of 2—17 carbon atoms, cycloalkyl of 3—6 carbon atoms, alkoxy of 1—4 carbon atoms, $—CH_2OCH_3$, $—CH_2OCH_2CH_3$, or —CH=CH—COOH;
X = hydrogen, fluorine, chlorine, bromine, methyl, or methoxy;
Y = hydrogen, fluorine, chlorine, bromine, methyl, or methoxy,

provided that when X and Y are both hydrogen, R_2 is not alkyl of 1—6 carbon atoms or cycloalkyl of 3—6 carbon atoms.

Novel compounds are those of the general formula (I) wherein (a) when R_1 is alkyl of 8—11 carbon atoms, at least one of X and Y is other than hydrogen; and (b) when R_1 is alkyl of 12—14 carbon atoms and X and Y are both hydrogen, R_2 cannot be alkyl of 1—6 carbon atoms or cycloalkyl of 3—6 carbon atoms. Further novel compounds of related structure are 3-acetoxy-2-(2-cyclohexylethyl)-1,4-naphthoquinone, 2-*n*-dodecyl-3-enanthyloxy-1,4-naphthoquinone and 3-acetoxy-2-(norborn-2-ylmethyl)-1,4-naphthoquinone. These novel compounds form a further aspect of our invention.

Included within the general formula (I) are those compounds wherein R_1 is straight chain alkyl of 12—14 carbon atoms and X and Y are hydrogen. The general formula also comprises compounds wherein at least one of X and Y is other than hydrogen and R_1 is e.g. alkyl of 11—14 carbon atoms, either branched or preferably straight chain; preferably either X or Y is hydrogen. Preferably R_2 is alkyl of 1—6 carbon atoms, alkenyl of 2—3 carbon atoms, methoxy or ethoxy and either X or Y is hydrogen. In particular R_2 may be methyl or ethyl and Y may be hydrogen.

Combination of the compounds used in this invention with other miticides often provides better total mite control than either material alone. Among such products which may be used advantageously with them are chlordimeform, formetanate ("Carzol"), propargite, tetradifon and benomyl. Most of such mixtures are novel.

The compounds of general formula (I) are miticides and aphicides. That is to say, when an effective amount of such compounds is brought into contact with mites or aphids, these pests are killed. The compounds are thus useful for protecting plants and animals from damage caused by mites or aphids.

The invention also includes miticidal and aphicidal compositions which contain at least one compound of the above formula as active ingredient and at least one of (a) a surface active agent, and (b) a solid or liquid diluent.

Preferred for their ease of synthesis are those compounds where R_1 is straight chain alkyl of 8—14 carbon atoms.

More preferred for their greater biological activity are those compounds where R_1 is straight chain alkyl of 12—14 carbon atoms; these compounds also have a direct lethal contact action against the eggs of mites. Mite eggs exposed to sprays of these compounds are killed and hatching fails to occur. Rates slightly higher than those used to kill the motile mite forms are generally required for good ovicidal effect.

It is preferred that R_2 is alkyl of 1—6 carbon atoms, more preferably straight chain of 1—6 carbon atoms, alkenyl of 2 or 3 carbon atoms, methoxy or ethoxy, most preferably ethyl or methyl. Specifically, the following compounds are preferred for use in our invention for their highest miticidal and aphicidal activity:

3-acetoxy-2-*n*-tetradecyl-1,4-naphthoquinone;
3-acetoxy-2-*n*-dodecyl-1,4-naphthoquinone;
3-propionyloxy-2-*n*-tetradecyl-1,4-naphthoquinone;
2-*n*-dodecyl-3-propionyloxy-1,4-naphthoquinone;
3-butyryloxy-2-*n*-tetradecyl-1,4-naphthoquinone;
2-*n*-dodecyl-3-methoxycarbonyloxy-1,4-naphthoquinone;
2-*n*-dodecyl-3-ethoxycarbonyloxy-1,4-naphthoquinone;
3-butyryloxy-2-*n*-dodecyl-1,4-naphthoquinone;
2-*n*-dodecyl-3-isobutyryloxy-1,4-naphthoquinone;
3-acetoxy-5-chloro-2-dodecyl-1,4-naphthoquinone.

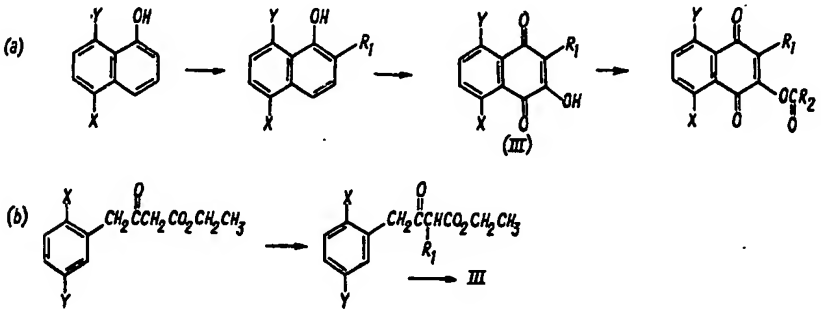
In a specific embodiment of the present invention, the compounds of the general formula (1) are applied in admixture with a Superior oil, preferably a minor amount of Superior oil, e.g., less than 5% by weight. The resulting miticidal activity is greater than the additive results. Superior oils are discussed in Chapman *et al. Selection of a Plant Spray Oil Combining Full Pesticidal Efficiency with Minimum Plant Injury Hazards*, Jour. Econ. Ent., 1962, 55:737-43. The resulting mixture of the compound of the above formula and Superior oil is though to be novel.

SYNTHESIS

Compounds of the general formula (I) can be prepared by the procedures

described in the previously cited *J. Am. Chem. Soc.* article and in U.S. Patent Nos. 2,553,647 and '648.

The compounds can be derived either (a) from the appropriately-substituted naphthol by the method taught in published German Offenlegungschrift #2,520,739, or (b) from the appropriate 4-phenyl-3-oxobutanoic ester as taught by Fieser, *et al.*, U.S.P. 2,553,647.



The final step in the synthesis may be accomplished by treating the corresponding 2-alkyl-3-hydroxy-1,4-naphthoquinone (III) with the appropriate acid chloride or anhydride in the presence of at least an equivalent of an amine such as pyridine or triethylamine, or by treating the salt of the 2-alkyl-3-hydroxy-1,4-naphthoquinone with the appropriate acid chloride or anhydride in an inert solvent.

The following Examples further illustrate processes for preparing these compounds. Examples 1, 3—6 and 8—11 are concerned with the preparation of intermediates.

EXAMPLE 1.

Preparation of the Sodium Salt of 2-*n*-Dodecyl-3-hydroxy-1,4-naphthoquinone

A dispersion of 1.9 parts of sodium hydride in 250 parts of tetrahydrofuran was added to a solution of 26 parts of 2-*n*-dodecyl-3-hydroxy-1,4-naphthoquinone in 450 parts of tetrahydrofuran at room temperature. The mixture was stirred at room temperature for 1 hour, then filtered to give a burgundy solution of the sodium salt.

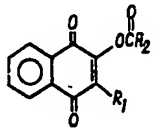
EXAMPLE 2.

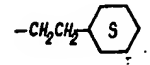
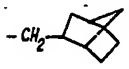
Preparation of 2-*n*-Dodecyl-3-methoxycarbonyloxy-1,4-naphthoquinone

Sixty parts of the above-mentioned sodium salt solution was stirred with 0.59 parts of methyl chloroformate in 10 parts of tetrahydrofuran at room temperature. The mixture was stirred for 1 hour, then allowed to stand overnight. The resulting suspension was filtered and the filtrate evaporated to dryness. The residue was crystallized from acetonitrile to give 2.0 parts of 2-*n*-dodecyl-3-methoxycarbonyloxy-1,4-naphthoquinone, m.p. 70—72°C.

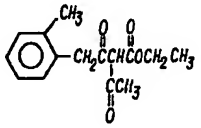
By using the appropriate 2-alkyl-3-hydroxy-1,4-naphthoquinone and the appropriate acid chloride or anhydride, the following compounds shown in Table I could be similarly prepared by anyone skilled in the art, using the procedure outlined in Examples 1 and 2 above or in Examples 1 and 2 of our copending Application 19705/75 (Serial No. 1,504,781).

TABLE 1



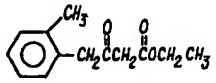
R_1	R_2	Melting Point (°C)
$-n\text{-}C_{12}H_{25}$	$-OCH_3$	70–72
$-n\text{-}C_{12}H_{25}$	$-OCH_2CH_3$	42–47
$-n\text{-}C_{12}H_{25}$	$-O-\overset{CH_3}{\overset{\vert}{C}}HCH_2CH_3$	[IR>=o 1753 cm^{-1}]
$-n-C_{12}H_{25}$	$-CH_2OCH_3$	69–71
$-n\text{-}C_{12}H_{25}$	$-CH_2OCH_2CH_3$	
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_7CH_3$	[IR>=o 1791 cm^{-1}]
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_{12}CH_3$	51–53
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_{16}CH_3$	
$-n\text{-}C_{12}H_{25}$	$-CH=CH_2$	
$-n\text{-}C_{12}H_{25}$	$-CH=CHCH_3$	43.5–44.5
$-n\text{-}C_{12}H_{25}$	$-\overset{CH_3}{\overset{\vert}{C}}=CH_2$	N_D^{25} 1.5202
$-n\text{-}C_{12}H_{25}$	$-CH=CH-CO_2H$	N_D^{25} 1.5162
$-n\text{-}C_{12}H_{25}$	$-CH=CH-CH=CH-CH_3$	68–74
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$	
	$-CH_3$	68–69
$n\text{-}C_{12}H_{25}$	$-(CH_2)_5CH_3$	N_D^{25} 1.5141
$n\text{-}C_{12}H_{25}$	$-(CH_2)_6CH_3$	54–57
	$-CH_3$	91–93
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_7-CH=CH-(CH_2)_7CH_3$	

EXAMPLE 3.
Preparation of Ethyl 2-Acetyl-4-(2-Methylphenyl)-3-oxobutanoate



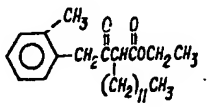
This material was prepared according to the procedure of M. Viscontini and N. Merckling, *Helvetica Chimica Acta, 35,* 2280 (1952). To 2.65 parts of magnesium turnings was added 15 parts absolute ethanol at room temperature and 0.5 parts of carbon tetrachloride. As soon as the initial reaction subsides 100 parts of dry ether was added. The mixture was stirred without cooling until the reaction ceased, then 19.6 parts of ethyl 3-oxobutanoate in 20 parts of dry ether was added with ice cooling and good stirring. After the resulting precipitate dissolved, the solution was cooled in an ice-salt bath and 16 parts of 2-methylphenylacetyl chloride was slowly added. The mixture was allowed to stand overnight at room temperature and then combined with ice and sulfuric acid. The ether layer was separated, washed with water, dried over sodium sulfate and stripped to give ethyl 2-acetyl-4-(2-methylphenyl)-3-oxobutanoate as a crude oil.

EXAMPLE 4.
Preparation of Ethyl 4-(2-Methylphenyl)-3-oxobutanoate



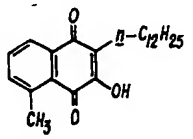
Following the method of Hunsdiecker *[Berichte, 75,* 454 (1942)*]*, 26 parts of ethyl 2-acetyl-4-(2-methylphenyl)-3-oxobutanoate was stirred for 10 hours at room temperature with 100 parts ethanol and 6.8 parts of sodium ethoxide. The mixture was diluted with water and extracted with ether. The solvent was then evaporated to give ethyl 4-(2-methylphenyl)-3-oxobutanoate.

EXAMPLE 5.
Preparation of Ethyl 2-[(2-Methylphenyl)acetyl]tetradecanoate



Three parts of ethyl 4-(2-methylphenyl)-3-oxobutanoate, 1 part of sodium methoxide, 4.6 parts of 1-bromododecane, 0.5 parts of potassium iodide and 50 parts of absolute ethanol were refluxed together for 4 hours and then stirred 18 hours at room temperature. The mixture was evaporated to a small volume, diluted with 100 parts water and extracted with ether. The ether extract was washed with saturated sodium bircarbonate, saturated sodium chloride solution and dried over magnesium sulfate. Evaporation of the ether gave 6 parts of crude ethyl 2-[(2-methylphenyl)-acetyl]tetradecanoate as an oil which was not further purified.

EXAMPLE 6.
Preparation of 2-Dodecyl-3-hydroxy-5-methyl-1,4-naphthoquinone

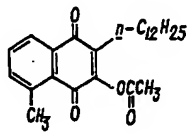


Four parts of crude ethyl 2-[(2-methylphenyl)-acetyl]tetradecanoate obtained in Example 5 was combined with 12 parts of cold concentrated sulfuric acid and stirred at room temperature for 66 hours. The mixture was poured into ice water

and made slightly basic by the addition of 50% aqueous sodium hydroxide. Enough ethanol was added to dissolve the organic matter and air was then bubbled through the solution for 3 hours. The resulting solution was extracted with 100 parts petroleum ether (twice), acidified with hydrochloric acid and re-extracted with diethylether. The ether extract was washed with saturated sodium chloride, dried over magnesium sulfate and evaporated. The residue was taken up in acetonitrile and filtered. The filtrate was evaporated to dryness and the residue triturated with petroleum ether to give 0.2 g of 2-dodecyl-3-hydroxyl-5-methyl-1,4-naphoquinone, m.p. 92—93°C.

EXAMPLE 7.

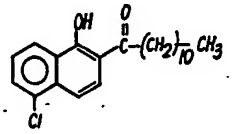
Preparation of 3-Acetoxy-2-dodecyl-5-methyl-1,4-naphthoquinone



3.8 Parts of 2-dodecyl-3-hydroxy-5-methyl-1,4-naphthoquinone, 8 parts of acetic anhydride and 32 parts of pyridine were stirred at room temperature for 16 hours. The resulting mixture was evaporated under reduced pressure to remove the pyridine. The residue was recrystallized from methanol to give 2.5 parts of 3-acetoxy-2-dodecyl-5-methyl-1-,4-naphthoquinone, m.p. 69—75°C.

EXAMPLE 8.

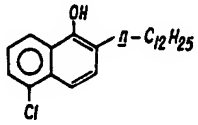
Preparation of 1-(5-Chloro-1-hydroxynaphthalen-2-yl)-1-dodecanone



A mixture of 16.6 parts of 5-chloro-1-naphthalenol [Erdmann and Kirchoff, *Liebig's* Ann., *247*, 372 (1888)] 19.2 parts of dodecanoic acid and 132 parts of boron trifluoride ether complex (48% BF_3) was stirred under nitrogen on a steam bath for 6 hours. Water (114 parts) was added and ether distilled off by further heating., The resulting mixture was cooled in ice and a tan solid was filtered and recrystallized from ethanol to give 18 parts of yellow 1-(5-chloro-1-hydroxynaphthalen-2-yl)-1-dodecanone, m.p. 86—87°C.

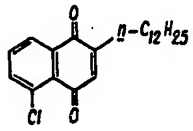
EXAMPLE 9.

Preparation of 5-Chloro-2-dodecyl-1-naphthalenol



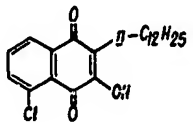
A solution of 17.4 parts of 1-(5-chloro-1-hydroxynaphthalen-2-yl)-1-dodecanone and 107 parts of 37% hydrochloric acid in 2.5 parts of ethanol was contacted with stirring at reflux during 26 hours, with 40 parts of zinc dust which has been amalgamated by treatment with 3 parts of mercuric chloride and 53 parts of 2.1% hydrochloric acid followed by washing with ethanol. The zinc amalgam was added in small portions throughout the reaction period. Upon cooling, a solid separated. After dissolution of this solid in ethanol, zinc amalgam was filtered, and cooling gave 0.5 parts of starting material which was filtered. Concentration of the filtrate, purification by recrystallization from ethanol, and column chromatography on silica gel using 1-chlorobutane as eluent gave 12 parts of 5-chloro-2-dodecyl-1-naphthalenol, m.p. 68—70°C.

EXAMPLE 10.
Preparation of 5-Chloro-2-dodecyl-1,4-naphthoquinone



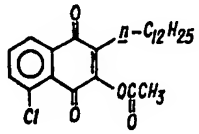
A mixture of 5.4 parts of 5-chloro-2-dodecyl-1-naphthalenol, 18 parts of 96% sulfuric acid, 71.5 parts of glacial acetic acid, and 29 parts of water was stirred at 70°C and 8.85 parts of cold 30% hydrogen peroxide was added dropwise over 8 hours. Stirring at 70°C was continued for another 17 hours. The mixture was cooled and an orange solid taken up in methylene chloride, and the extract washed with water, dried and stripped. The resulting tan solid was purified by column chromatography from 1-chlorotutane on silica gel to give 2 parts of 5-chloro-2-dodecyl-1,4-naphthoquinone, m.p. 57.5—585°C.

EXAMPLE 11.
Preparation of 5-Chloro-2-dodecyl-3-hydroxy-1,4-naphthoquinone



A mixture of 1.7 parts of 5-chloro-2-dodecyl-1,4-naphthoquinone, 25 parts ethanol, 0.626 parts anhydrous sodium carbonate and 6.3 parts water was contacted with 1.13 parts of 30% hydrogen peroxide at 32°C and then refluxed for 10 minutes. The resulting mixture was then cooled to 50°C and a solution of 1.56 parts of potassium hydroxide in 49.5 parts of ethanol was added to it. The resulting deep red mixture was then heated to 50°C over 25 minutes and the temperature held there for 45 minutes. After cooling to 10°C the mixture was then contacted with 251 parts of 2.72% hydrochloric acid. The resulting yellow crystals were filtered, dried and purified by column chromatography on silica gel using 1-chlorobutane as eluent. Solvent removal gave 1.4 parts of 5-chloro-2-dodecyl-3-hydroxy-1,4-naphthoquinone, m.p. 102—104.5°C.

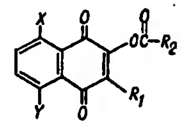
EXAMPLE 12.
Preparation of 3-Acetoxy-5-chloro-2-dodecyl-1,4-naphthoquinone



A solutionof 0.95 parts of 5-chloro-2-dodecyl-3-hydroxy-1,4-naphthoquinone in 20 parts of anhydrous tetrahydrofuran was added under nitrogen to a mixture of 0.0635 parts of dispersed sodium hydride in 40 parts of tetrahydrofuran with stirring at room temperature. After 45 minutes of stirring, a solution of 0.275 parts of acetyl chloride in 30 parts of tetrahydrofuran was added and the mixture stirred for 5 hours. The tetrahydrofuran was stripped under reduced pressure and the residue taken up in methylene chloride and then washed with water, 10% hydrochloric acid, four more times with water, dried over sodium sulfate and stripped. The resulting yellow solid was purified by column chromatography on silica gel using 1-chlorobutane as eluent. Solvent removal gave 0.9 parts of 3-acetoxy-5-chloro-2-dodecyl-1,4-naphthoquinone, m.p. 57—59°C.

By using the appropriate 2-alkyl-3-hydroxy-1,4-naphthoquinone and the appropriate acid chloride or anhydride, the following compounds shown in Table 2 could be similarly prepared by anyone skilled in the art, using the procedure outlined in Examples 3 to 12.

TABLE 2



(I)

R_1	R_2	X	Y	Melting Point C)
$-n\text{-}C_8H_{17}$	$-CH_2CH_2CH_3$	Cl	H	—
$-n\text{-}C_8H_{17}$	$-CH_3$	CH_3	H	—
$-s\text{-}C_8H_{17}$	$-CH_3$	Cl	Cl	—
$-(CH_2)_4-$(S)	$-CH_3$	Cl	H	—
$-n\text{-}C_{11}H_{23}$	$-CH_3$	Cl	H	—
$-n\text{-}C_{11}H_{23}$	$-CH_2CH_2CH_3$	Cl	CH_3	—
$-n\text{-}C_{11}H_{23}$	$-OCH_3$	OCH_3	H	—
$-n\text{-}C_{12}H_{25}$	$-CH_2OCH_3$	Br	H	—
$-n\text{-}C_{12}H_{25}$	$-CH_3$	Cl	OCH_3	—
$-n\text{-}C_{12}H_{25}$	$-CH_2OCH_2CH_3$	H	Cl	—
$-s\text{-}C_{12}H_{25}$	$-CH{<}\begin{smallmatrix}CH_2\\ \vert\\ CH_2\end{smallmatrix}$	Cl	Br	—

TABLE 2 (Continued)

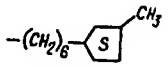
R_1	R_2	X	Y	Melting Point C)
	$-OCH_3$	Cl	H	–
$-n\text{-}C_{12}H_{25}$		Br	H	–
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_4CH_3$	F	H	–
$-n\text{-}C_{12}H_{25}$	$-C(CH_3)_3$	Cl	F	–
$-n\text{-}C_{13}H_{27}$	$-OCH_2CH_3$	CH_3	CH_3	–
$-n\text{-}C_{12}H_{25}$	$-O-\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2CH_3$	Cl	H	–
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_{16}CH_3$	Cl	H	–
$-n\text{-}C_{12}H_{25}$	$-CH=CH_2$	Br	CH_3	–
$-n\text{-}C_{12}H_{25}$	$-CH=CHCH_3$	Br	F	–
$-n\text{-}C_{12}H_{25}$	$-\underset{\displaystyle CH_3}{\underset{\vert}{C}}H=CH_2$	OCH_3	Br	–
$-n\text{-}C_{12}H_{25}$	$-CH=CHCO_2H$	Cl	H	–

TABLE 2 (Continued)

R_1	R_2	X	Y	Melting Point (°C)
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3$	Cl	H	–
$-n\text{-}C_{12}H_{25}$	$-(CH_2)_7CH{=}CH(CH_2)_7CH_3$	Cl	H	–
$-n\text{-}C_{14}H_{29}$	$-CH_3$	OCH_3	OCH_3	–
$-s\text{-}C_{14}H_{29}$	$-CH_2CH_3$	H	CH_3	–
$-(CH_2)_8-C_6H_5$	$-CH{=}CHCH_3$	Cl	H	–
$-n\text{-}C_{10}H_{21}$	$-CH_3$	Cl	H	–
$-n\text{-}C_{12}H_{25}$	$-CH_3$	Br	Br	–
$-n\text{-}C_{12}H_{25}$	$-CH_3$	H	F	–
$-n\text{-}C_{12}H_{25}$	$-CH_3$	H	OCH_3	–
$-n\text{-}C_{12}H_{25}$	$-CH_3$	H	Br	–
$-n\text{-}C_{12}H_{25}$	$-CH_3$	Br	H	&

Formulation and Use

These compounds are useful as miticides and can be used to protect both plants and animals from damage caused by these pests. More specifically, fruits, field crops, vegetables, ornamentals, birds and other warm-blooded animals including man can also be protected.

When mites come into contact with these compounds, either in the form of direct sprays or by walking over surfaces which have been treated, they rapidly become irritated and leave the area or are killed if they have been exposed to a sufficiently high dosage. While most plants or animals are able to tolerate the presence of very small numbers of mites without apparent adverse effect, the reproductive capacity of these pests is enormous. Generally, mite populations rapidly build up, easily out-stripping parasite and predator capabilities for control. Growers noting rapid mite build-up must take immediate action to prevent

damage to economically important crops. Thus, a method is needed for immediately reducing mite build-up and thereby preventing damage to important crops.

The compounds of this invention also have a direct lethal contact action against the eggs of mites. Mite eggs exposed to sprays of these compounds are killed and hatching fails to occur. Rates slightly higher than those used to kill the motile mite forms are generally required for good ovicidal effect.

These compounds are most effective for the control of mites. Very small quantities of these compounds are required for miticidal activity; additionally, the compounds are not rapidly washed from leaves by rain. At typical rates of use, they do not have any adverse effect on ladybird beetles, which are important mite predators, and the compounds rapidly degrade in the environment. The compounds are also effective against organophosphorous-resistant strains of mites.

The quantity of compound needed for miticidal activity will vary depending on the specific situation. Among the variables that must be considered in deciding on the quantity of chemical to be used are the specific compound itself, the specific mite to be controlled, weather conditions, the type of crop, the stage of development of the crop, the volume of spray applied, population pressure, and the interval between applications. For plant protection, solutions or suspensions containing as little as 5 ppm of active ingredient in a spray solution may prove effective under a given set of circumstances. For field usage, however, in high-volume applications, aqueous spray preparation containing 40—4,000 ppm of active ingredient are generally useful. Preferred are suspensions containing 80—1,000 ppm, and most preferred are those containing 150—500 ppm. On an area basis, in general, .03 to 15 kilograms of active ingredient per hectare are acceptable, preferably .06 to 8 kilograms, and most preferably 1 to 4 kg. When applied in an orchard, spraying is continued until run-off is observed.

It may be desirable or useful to mix the compounds of this invention with other agricultural pesticides or adjuvants. Such mixtures often increase the effectiveness of the application on mites and broaden the scope of control to embrance other pests such as insects, fungi, nematodes, or bacteria. A mixture with a refined petroleum spray oil or Superior oil has been shown to provide greater than additive results on mites. Other pesticides with which the compounds of this invention may be mixed to achieve broader-spectrum activity include:

diazinon	— 0,0-diethyl 0-(2-isopropyl-4-methyl-6-pyrimidyl)phosphorothioate
disulfoton	— 0,0-diethyl S-2(ethylthio)ethyl-phosphorodithioate
phorate	— 0,0-diethyl S-(ethylthio)methylphos-phorodithioate
oxamyl	— S-methyl 1-(diamethylcarbamoyl-N-[(methylcarbamoyl)oxy]thioformimidate
methomyl	— S-methyl N-(methylcarbamoyloxy)thio-acetimidate
benomyl	— 1-butylcarbamoyl-2-benzimidazole-carbamic acid, methyl ester
captan	— N-trichloromethylthiophthalimide
maneb	— ethylenebisdithiocarbamic acid, manganese salt
carboxin	— 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide
streptomycin	— 2,4-diguanidino-3,5,6-trihydroxycyclo-hexyl-5-deoxy-2-*o*-(2-deoxy-2-methylamino)-*α*-glycopyranosyl-3-formylpentofuranoside
azinphosmethyl	— 0,0-dimethyl-*S*-[4-oxo-1,2,3-benzo-triazin-3-(4H)ylmethyl]phosphorodi-thioate.

The compounds are especially suited for the protection of living plants such as fruit-bearing trees, nut-bearing trees, ornamental trees, forest trees, vegetable crops, horicultural crops (including ornamentals, small fruit and berries) and grain and seed crops. Apple trees, peach trees, cotton, citrus trees, beans and peanuts

are particularly susceptible to mite damage and can be protected by application of the compounds of this invention. To assure control throughout the growing season (e.g., June to August in the Northern Hemisphere) multiple applications at desired intervals can be utilized.

Many species of mites are controlled by the compounds of this invention. The following is a list of representative susceptible mites along with the types of damage that they can cause: *Panonychus ulmi* (European red mite) and *Tetranychus urticae* (two-spotted mite) which are commonly called "orchard mites", and which attack a great many deciduous trees, such as apple, pear, cherry, plum and peach trees; *Tetranychus atlanticus* (Atlantic or strawberry mite), *T. cinnabarinus* (carmine) spider mite) and *T. pacificus* (Pacific mite); which attack cotton and numerous other crop plants; *Paratetranchus citri* (citrus red mite) and others which attack citrus; *Phyllocoptruta oleivora* which causes citrus rust; *Bryobia praetiosa* (clover mite) which atacks clover, alfalfa and other crops; *Aceria neocynodomis* which attacks grasses and other plants; *Tetranychus medanieli* which attacks deciduous fruit in northwestern U.S.; and *Oligonychus pratensis* which attacks sorghum and other grasses.

Useful formulations of thhese compounds can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders and emulsifiable concentrates. Many of these may be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from a few pints to several hundred gallons per acre. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

TABLE 3

	Active Ingredient	Diluent(s)	Surfactant(s)
Wettable Powders	20–90	0–74	1–10
Oil Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5–50	40–95	0–15
Aqueous Suspensions	10–50	40–84	1–20
Dusts	1–25	70–99	0–5
Granules & Pellets	1–95	5–99	0–15
High-strength Compositions	90–99	0–10	0–2

Lower or higher levels of active ingredients can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins et al. "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, N. J. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide", 2nd Edn., Inter-science, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual", Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, "Encylopedia of Surface Active Agents", Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can

contain minor amounts of additives e.g. to reduce foam, caking, corrosion or microbiological growth.

The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine, solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Suspensions are prepared by wet-milling (see, i.e., Littler U.S. Patent 3,060,084). Granules and pellets may be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See J. E. Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp. 147 ff. and Perry's *Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, N.Y., 1963, pp. 8—59 ff.

For further information regarding the art of formulation, see, for example:

J. B. Buchanan, U.S. Patent 3,576,834 April 27, 1971, Col. 5, Line 36 through Col. 7, Line 70 and Exs. 1—4, 17, 106, 123—140.

R. R. Shaffer, U.S. Patent 3,560,616 February 2, 1971, Col. 3, Line 48 through Col. 7, Line 26 and Examples 3—9, 11—18.

E. Somers, "Formulation", Chapter 6 in Torgeson, "Fungicides", Vol. I, Academic Press, N. Y. 1967.

Still another liquid formulation which is particularly convenient for small-scale use is the "aerosol" formulation which is packaged under pressure in a suitable container. The active ingredient may be present in a suspension, emulsion or solution. For simplicity in preparation and use, solutions are preferred. The pressure may be supplied by low-boiling liquids such as propane or chlorofluoro carbons or by relatively soluble gases such as carbon dioxide or nitrous oxide. The chloro-fluoro carbons are preferred for a combination of good solvent power and lack of flammability.

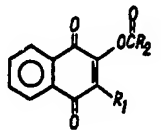
Miticidal ability of these compounds is illustrated in the following examples:

EXAMPLE 13.

Test units consisting of plant pots containing two red kidney bean plants in the 2-leaf stage were infested with 2-spotted mites and sprayed to run-off with solutions/suspensions of the compounds of this invention. Solutions/suspensions were made by dissolving weighed quantities of the active ingredients in 10 ml of acetone and then diluting to volume with water containing TREM 014 at 1:3000. Mortality was evaluated two days after spraying.

TABLE 4

Compounds



R_1	R_2	% Mortality at .002% Spray Concentrations
n-$C_{12}H_{25}$	$-(C_2)_7CH_3$	96
n-$C_{12}H_{25}$	$-(CH_2)_{12}CH_3$	99
n-$C_{12}H_{25}$	$-CH=CHCH_3$	100
n-$C_{12}H_{25}$	$-CH=CHCH=CHCH_3$	98
n-$C_{12}H_{25}$	$-OCH_3$	100
n-$C_{12}H_{25}$	$-OC_2H_5$	99
n-$C_{12}H_{25}$	$-CH_2-O-CH_3$	97
n-$C_{12}H_{25}$	$-CH=CHCOOH$	100
n-$C_{12}H_{25}$	$-OCHCH_2CH_3$ (with CH_3 branch)	60

EXAMPLE 14.

Test units consisting of plant pots containing two red kidney beans in the 2-leaf stage were infested with 2-spotted mites and sprayed to run-off with dispersions of 3-acetoxy-5-chloro-2-dodecyl-1,4-naphthoquinone at various rates. Dispersions were made by dissolving an appropriately weighed quantity of the active ingredient in 10 ml of acetone and then diluting with water containing TREM 014 at 1:3000. Mortality was evaluated 2 days after spraying. A table of results is set forth below:

Concentration of Active Ingredient (ppm)	% Mortality (24 hours)
500	100
50	100
20	100
10	100
5	100
2.5	88

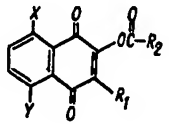
EXAMPLE 15.

Red kidney bean plants in the 2-leaf stage were infested with mites which were allowed to oviposit. About 24 hours later the leaves were dipped in tetraethyl pyrophosphate solution to kill the mites. After drying, the plants were sprayed with test dispersions of 3-acetoxy-5-chloro-2-dodecyl-1,4-naphthoquinone at various rates. Dispersions were made by dissolving an appropriately weighed quantity of the active ingredient in 10 ml of acetone and then diluting with water containing TREM 014 at 1:3000. Hatching activity was observed and results were recorded five days later.

Concentration of Active Ingredient (ppm)	% Ovicidal Activity (5 days)
100	100
50	100
25	98
12.5	79
Control (0)	1

WHAT WE CLAIM IS:—

1. A method for controlling mites or aphids which comprises applying to a locus infested or liable to be infested with said mites or aphids an effective amount of a compound of the general formula



(I)

wherein

R_1 = alkyl of 8—14 carbon atoms either branched, cyclic, or straight chained;
R_2 = alkyl of 1—17 carbon atoms either branched or straight chained, alkenyl of 2—17 carbon atoms, cycloalkyl of 3—6 carbon atoms, alkoxy of 1—4 carbon atoms, $—CH_2OCH_3$, $—CH_2OCH_2CH_3$, or —CH=CH—COOH;
X = hydrogen, fluorine, chlorine, bromine, methyl, or methoxy;
Y = hydrogen, fluorine, chlorine, bromine, methyl or methoxy; provided that when X and Y are both hydrogen, R_2 is not alkyl of 1—6 carbon atoms or cycloalkyl of 3—6 carbon atoms.

2. The method of claim 1 wherein R_1 is straight chain alkyl of 12—14 carbon atoms and X and Y are hydrogen.

3. The method of claim 2 wherein R_2 is alkenyl of 2 or 3 carbon atoms, methoxy or ethoxy.

4. The method of claim 1 wherein at least one of X and Y is other than hydrogen.

5. The method of claim 4 wherein R_1 is alkyl of 11—14 carbon atoms, either branched or straight chain.

6. The method of claim 4 or 5 wherein R_2 is alkyl of 1—6 carbon atoms, , alkenyl of 2 or 3 carbon atoms, methoxy or ethoxy.

7. The method of any of claims 4—6 wherein either X or Y is hydrogen.

8. The method of any of claims 5—7 wherein R_1 is straight chain alkyl of 11—14 carbon atoms.

9. The method of any of claims 4—8 wherein R_2 is methyl or ethyl.

10. The method of claims 5, 6, 7, 8 and 9.

11. The method of claims 8 and 9 wherein Y is hydrogen.

12. The method of claim 11 wherein said compound is 3-acetoxy-5-chloro-2-*n*-dodecyl-1,4-naphthoquinone.

13. The method of claim 1 wherein said compound is 2-*n*-dodecyl-3-methoxycarbonyloxy-1,4-naphthoquinone.

14. The method of claim 1 wherein said compound is 2-*n*-dodecyl-3-ethoxycarbonyloxy-1,4-naphthoquinone.

15. The method of any of the preceding claims wherein said compound is employed in combination with chlordimeform, formetanate, propargite, tetradifon or benomyl.

16. The method of any of the preceding claims wherein said locus is a plant.

17. The method of claim 16 wherein said compound is applied at a rate of 0.1 to 4 kg/ha.

18. The method of any of the preceding claims wherein said compound is applied together with a Superior Oil.

19. The method of claim 1, substantially as hereinbefore described.

20. The method of claim 1, substantially as hereinbefore described with reference to the Examples herein.

21. A composition for the control of mites or aphids comprising a compound

of general formula (I) as defined in claim 1 and at least one of (a) a surface active agent, and (b) a solid or liquid diluent.

22. The composition of claim 21 wherein said compound is as defined in any of claims 2—11.

23. The composition of claim 21 wherein said compound is as defined in claim 12, 13 or 14.

24. The composition of claim 21, 22 or 23 including a Superior Oil.

25. The composition of any of claims 21—24 including chlordimeform, formetanate, propargite, tetradifon or benomyl.

26. The composition of claim 21, substantially as hereinbefore described with reference to the Examples.

27. A compound of the formula (I) wherein R_1 = alkyl of 8—14 carbon atoms either branched, cyclic, or straight chain;
R_2 = alkyl of 1—17 carbon atoms either branched or straight chain, alkenyl of 2—17 carbon atoms, cycloalkyl of 3—6 carbon atoms, alkoxy or 1—4 carbon atoms, $—CH_2OCH_3$, $—CH_2OCH_2CH_3$, or —CH=CH—COOH;
X = hydrogen, fluorine, chlorine, bromine, methyl or methoxy;
Y = hydrogen, fluorine, chlorine, bromine, methyl, or methoxy;
provided, (a) when R_1 is alkyl of 8—11 carbon atoms, at least one of X and Y is other than hydrogen; and (b) when R_1 is alkyl of 12—14 carbon atoms and X and Y are both hydrogen, R_2 cannot be alkyl of 1—6 carbon atoms or cycloalkyl of 3—6 carbon atoms.

28. The compounds of claim 27 wherein R_1 is straight chain alkyl of 12—14 carbon atoms, and X and Y = hydrogen.

29. The compound of claim 28 wherein R_2 is alkenyl of 2 or 3 carbon atoms, methoxy or ethoxy.

30. The compound of claim 27 wherein at least one of X and Y is other than hydrogen.

31. The compound of claim 30 wherein R_1 is alkyl of 11—14 carbon atoms, either branched or straight chain.

32. The compound of claim 30 or 31 wherein R_2 is alkyl of 1—6 carbon atoms, alkenyl of 2 or 3 carbon atoms, methoxy or ethoxy.

33. The compound of claim 30 wherein either X or Y is hydrogen.

34. The compound of claim 31, 32 or 33 wherein R_1 is straight chain alkyl of 11—14 carbon atoms.

35. The compound of any of claims 30—34 wherein R_2 is methyl or ethyl.

36. The compound of claim 31 or 34 wherein R_2 is alkyl of 1—6 carbon atoms, alkenyl of 2—3 carbon atoms; methoxy or ethoxy; and either X or Y is hydrogen.

37. The compound of claim 36 wherein R_2 is methyl or ethyl.

38. The compound of claim 34 wherein R_2 is methyl or ethyl; and Y is hydrogen.

39. 3-Acetoxy-5-chloro-2-*n*-dodecyl-1,4-naphthoquinone.

40. 2-*n*-Dodecyl-3-methoxycarbonyloxy-1,4-naphthoquinone.

41. 2-*n*-Dodecyl-3-ethoxycarbonyloxy-1,4-naphthoquinone.

42. Compounds of claim 27 as hereinbefore specifically disclosed excepting the compound of claims 39—41.

43. Compounds of claim 27 substantially as hereinbefore described.

44. A mixture of a compound of any of claims 27—43 with a Superior Oil.

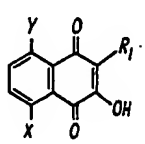
45. A mixture of a compound of any of claims 27—43 with chlordimeform, fometanate, propargite, tetradifon or benomyl.

46. 3-Acetoxy-2-(2-cyclohexylethyl)-1,4-naphthoquinone.

47. 2-*n*-Dodecyl-3-enanthyloxy-1,4-naphthoquinone.

48. 3-Acetoxy-2-(norborn-2-ylmethyl)-1,4-naphthoquinone.

49. A process for the preparation of a compound of claim 27 which comprises (a) treating a corresponding 2-alkyl-3-hydroxy-1,4-naphthoquinone of general formula



(III)

with the appropriate acid chloride or anhydride in the presence of at least an equivalent of an amine; or (b) treating a salt of said compound of general formula

(III) with the appropriate acid chloride or anhydride in an inert solvent.

50. The process of claim 49, substantially as hereinbefore described with reference to Examples 1—12 herein.

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